Very-low-temperature molecular beam epitaxial growth of GaP/AlAs heterostructures for distributed Bragg reflector applications

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Using very-low-temperature (VLT) molecular beam epitaxy (MBE), (Ga,P)/(Al,As) heterostructures were grown for use in a distributed Bragg reflector (DBR). Through the use of VLT MBE and control of the group-V overpressure, the microstructure can be controlled resulting in either amorphous or polycrystalline material for both materials. Also, the growth rate is highly dependent on the group-V overpressure due to the high sticking coefficients of both As and P at these low growth temperatures. Using lateral oxidation, the amorphous AlAs was converted to its oxide for use in a visible wavelength DBR. Variabilities within layer thickness, especially the amorphous AlAs layers, were investigated to determine their effect on the DBR reflectivities. Different DBR designs were employed resulting in a double passband DBR which is highly reflective at wavelengths of both 550 and 1100 nm. © *2001 American Vacuum Society.*
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I. INTRODUCTION

Growth of high-quality, lattice-mismatched materials is of particular interest for various device applications. Much effort has been dedicated to the pursuit of compliant epitaxy techniques with limited success. For optical devices, such as vertical cavity surface emitting lasers and resonant-cavity light emitting diodes, highly reflective mirrors using distributed Bragg reflectors (DBRs) are required for device performance. The GaAs/AlAs material system is preferred for the fabrication of the DBRs due to the large index difference of the material and the ability to laterally wet oxidize the AlAs to form semiconductor/oxide DBRs.[1,2] Lattice matching limits the use of this material system to GaAs-based structures thereby preventing the fabrication of semiconductor/oxide mirrors for long- or short-wavelength applications. Alternative techniques, such as electron beam evaporation, can be used to form the DBR mirrors, but DBRs formed using this technique often have increased interfacial roughness which can increase scattering losses.[3] Therefore an alternative method for the easy fabrication of highly reflective semiconductor/oxide DBR mirrors is needed.

Using very-low-temperature molecular beam epitaxial (VLT MBE) growth techniques, the GaAs/AlAs material system has been used to fabricate a substrate independent DBR for use in long-wavelength applications.[4] The microstructure of the material can be manipulated between polycrystalline and amorphous (α) materials by simply controlling the As overpressure. Due to the lack of crystal structure in amorphous material, we can use these materials on any host substrate without generating dislocations. While a GaAs/AlAs DBR is suitable for near infrared long-wavelength applications, its use in the visible spectrum would be problematic because of absorption of the high-energy photons in GaAs. This problem can be solved by replacing GaAs with a large band-gap material, such as GaP. Due to the compliant nature of the VLT MBE deposited material, an amorphous or polycrystalline (Ga,P)/Al-oxide DBR could be used in nitride-based devices which operate in the blue, green, and yellow regions of the visible spectrum.

In this study the effects of phosphorus overpressure on the microstructure and the growth rate of (Ga,P) were investigated. Visible wavelength polycrystalline (Ga,P)/Al-oxide DBRs were fabricated and characterized. It was determined that the layer thickness of the AlAs was difficult to control. Examination of this phenomenon and its effects on the reflectivity of the DBRs were also investigated. Finally, a unique two-wavelength (λ) DBR, one falling in the visible spectrum and the other in the infrared spectrum, has been designed and fabricated using VLT MBE grown polycrystalline (Ga,P) and lateral oxidation of α-(Al,As).

II. EXPERIMENT

In this study we used VLT MBE techniques to deposit alternating layers of (Ga,P) and α-(Al,As) to form the structure for the DBR. The samples were grown in an all solid-source MBE chamber using valved As and P cracking cells. Following a previous study, it was known that the group-V overpressure could affect the microstructure of VLT-grown GaAs and AlAs.[4] To determine the effects of phosphorus overpressure during the growth on the microstructure of (Ga,P) material, a sample was grown employing alternating layers of α-(Al,As) and (Ga,P) where the P overpressure was changed for each (Ga,P) layer. The α-AlAs layers were grown at 1.5×10^{-6} Torr, a pressure known to result in amorphous material. At a substrate temperature of ~100 °C, as measured by a thermocouple located at the rear of the sample, the layers were deposited at a rate of 0.5 monolayers (ML)/s. The phosphorus overpressure used in the three (Ga,P) layers was 1.5×10^{-6}, 7×10^{-7}, and 4×10^{-7} Torr as measured by an ion gauge flux monitor located near the

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growth position. Cross sectional transmission electron microscopy (XTEM) was used to determine the growth rate and the microstructure of the (Ga,P). In addition, Auger electron spectroscopy (AES) was used to estimate the amount of phosphorus in the (Ga,P) layers.

Using the information about the microstructure, growth rate, and lateral oxidation rate of the α-(AlAs),[4,5] a DBR structure was designed and fabricated to reflect at a central wavelength of 550 nm. The α-(Al,As) was oxidized using a horizontal, open-tube furnace at 450 °C. The water vapor was supplied to the samples using a nitrogen carrier gas which was bubbled through a water reservoir kept at a temperature of 85 °C. The reflectivity spectrum of the DBR was measured by a spectrophotometer at a near normal incident angle of 7°. Using tungsten and deuterium lamps, the spectrophotometer provides a measurable spectral range of 0.175–3.3 μm. The reflectivity data were obtained by comparing the reflection from the DBR sample to the reference beam in a double-beam configuration.

III. EXPERIMENTAL RESULTS

A. Control of material microstructure

From the previously study,[4] the effect of As overpressure on the structure of AlAs was known. To determine the effects of the phosphorus overpressure on the microstructure of GaP, a heterostructure sample was grown with different overpressures for the (Ga,P) layers. During growth of the (Ga,P) Layers, reflection high-energy electron-diffraction (RHEED) patterns were monitored. The layer grown with the highest overpressure, 1.5×10^{-6} Torr, showed a RHEED pattern with a featureless-diffuse pattern indicating an amorphous material. The layers grown with lower overpressures had a faint ring structure indicating the possibility of polycrystalline growth. The difference in the microstructure of the (Ga,P) layers is due to the presence of excess phosphorus in the film grown at the higher overpressure. At these low growth temperatures, the excess phosphorus atoms stick to the surface, surrounding the Ga atoms, thus masking the crystalline structure. For phosphorus overpressures near or greater than 1.5×10^{-6} Torr, there is a sufficient amount of phosphorus to prevent crystalline growth, which induces amorphous material. For samples grown with lower phosphorus overpressures, this effect is lessened allowing for more crystalline structure to be maintained. But, at such low substrate temperatures, the mobility of the adatoms is not large enough to result in single-crystal growth.

Using XTEM, it was determined that the phosphorus overpressure had a great effect on the microstructure of GaP as well as the layer thickness. The layer grown at 1.5×10^{-6} Torr showed an amorphous microstructure and a higher growth rate, 1.44 Å/s as seen in Fig. 1(a), than the other two overpressures used. The layer grown at an overpressure of 7×10^{-7} Torr showed a polycrystalline material with small grain size and a growth rate of 1.13 Å/s. Finally, the layer grown with the lowest overpressure was of a polycrystalline nature and had a rough surface morphology. In addition, this last layer had the slowest growth rate at 0.63 Å/s. Included in Fig. 1(a) is a line indicating the growth rate of single-crystal GaP according to RHEED intensity oscillations. Notice that the growth rate of the two layers grown at the two lower overpressures is lower than the single-crystal growth rate.

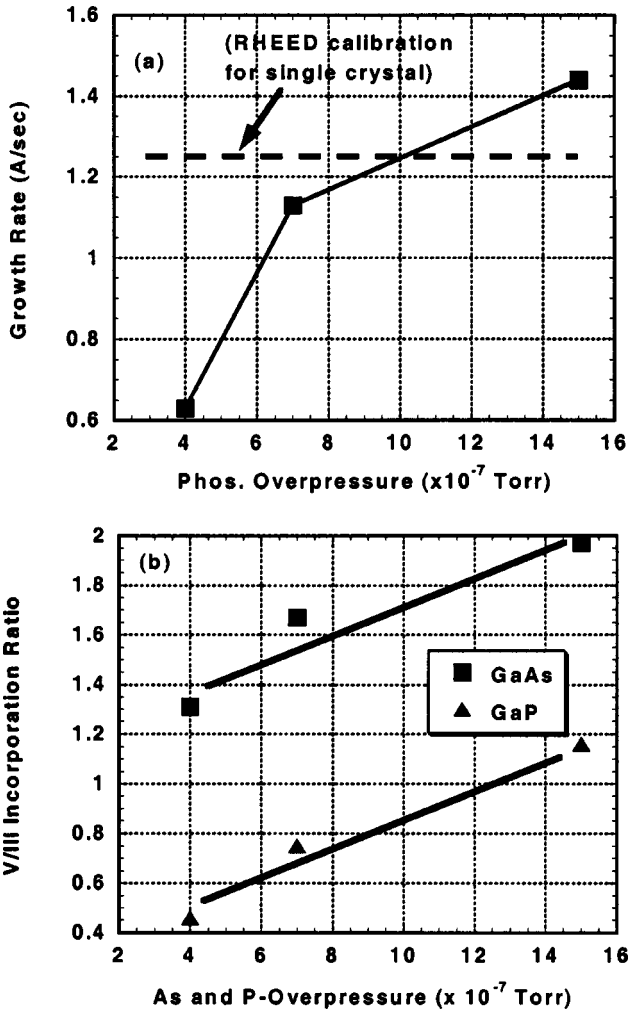

FIG. 1. (a) Growth rate of VLT (Ga,P) as a function of phosphorus overpressure. Note that the growth rate is highly dependent on the overpressure due to the low temperatures used in the growth. The dashed line is the measured growth rate of single-crystal GaP using RHEED oscillations. (b) AES data for the V/III incorporation ratio in both VLT-grown (Ga,As) and (Ga,P) films. Note that only at the highest overpressure does the V/III ratio of (Ga,P) exceed one. The difference in the incorporation ratio between the two materials is due to the difference in the sticking coefficients of the two group-V species.

To further investigate the amount of phosphorus in the (Ga,P) films, Auger electron spectroscopy (AES) was used. As can be seen in Fig. 1(b), the V/III incorporation ratio increases as the P overpressure is increased as expected. For comparison, the data for VLT-GaAs has been included.[4] Note that the V/III ratio is greater than 1 for the (Ga,As) material grown at all As overpressures and it is less than 1 for the two lowest overpressures used in the growth of the (Ga,P) layers. In fact, we have excess Ga in these films as opposed to excess As as seen in the (Ga,As) layers. Only at a phosphorus overpressure of 1.5×10^{-6} Torr does the V/III

ratio become greater than 1. Unlike growth at normal substrate temperatures, where the sticking coefficient of the group-V elements is primarily determined by the arrival rate of the group-III atom, the sticking coefficient of the group-V species is drastically increased at these low growth temperatures. This causes a strong dependence of the growth rate on group-V overpressure. The microstructure correspondingly changes from polycrystalline to amorphous as the V/III incorporation ratio exceeds 1. The difference between the incorporation ratios between the As- and P-based materials is due to the higher vapor pressure of the phosphorus.[6] The phosphorus sticking coefficient, while increased at lower temperatures, is still below that of As causing a reduction in the amount of group-V species in these films.

B. Growth and fabrication of the DBR

With the information concerning the growth rate of the polycrystalline GaP and α-AlAs and lateral oxidation rate calibrations, a DBR was designed to reflect at a central wavelength of 550 nm. To approximate the index of refraction (n) of polycrystalline (Ga,P) at these wavelengths, we used data for single-crystal GaP which was 3.44 at a wavelength of 550 nm.[7] The index of refraction for the Al-oxide was estimated to be 1.35 using XTEM and ellipsometry measurements. Taking into account the effects of excess As as well as the volume contraction upon conversion of α-AlAs to Al-oxide, a 6 pair 400 Å polycrystalline (Ga,P)/1132 Å α-AlAs DBR structure was grown. A phosphorus overpressure of 7×10^{-7} Torr was chosen to ensure polycrystalline material. Polycrystalline material was chosen because of its stronger resistance to oxidation when compared to amorphous material. The samples were patterned into 5 μm trenches spaced 120 μm apart using standard photolithography. Reactive ion etching using a $SiCl_4$/Ar gas mixture was then employed to cut trenches into the structure. The samples were then immediately loaded into an open tube furnace for lateral oxidation. An oxidation time of 90 min was chosen to ensure that the sample was fully oxidized and to account for any changes in oxidation rate due to the geometry of the pattern of the sample.

Using a spectrophotometer and a broadband light source the reflectivity spectrum of the DBR was measured. Shown in Fig. 2(a) is the reflectivity spectrum for the DBR as well as a spectrum for the simulated DBR. The simulated reflectivity curve was based on the measured thicknesses of the layers using XTEM. As seen in the figure, the bandwidth of the DBR was found to be close to that of the simulated case, but the maximum reflectivity is lower. Possible causes of the lower reflectivity include scattering losses due to rough interfaces, thickness variations, and absorption of the photons in the DBR. To investigate the possibility of thickness variation, XTEM was performed on the as-grown sample to determine the individual layer thicknesses. The polycrystalline (Ga,P) layers were found to be very uniform and matched the designed thickness very well. The (Al,As) layers, however, showed variability. Figure 2(b) shows the percent difference of the (Al,As) layers as compared to the designed thicknesses. Note that the (Al,As) layer thickness varied as much as 30% which would have obvious effects on the reflectivity spectrum. An 11 pair DBR was grown using the same layer thicknesses to increase the overall reflectivity, but with no success. The maximum reflectivity was near that of the 6 pair DBR and XTEM indicated similar variabilities of the (Al,As) layer thicknesses.

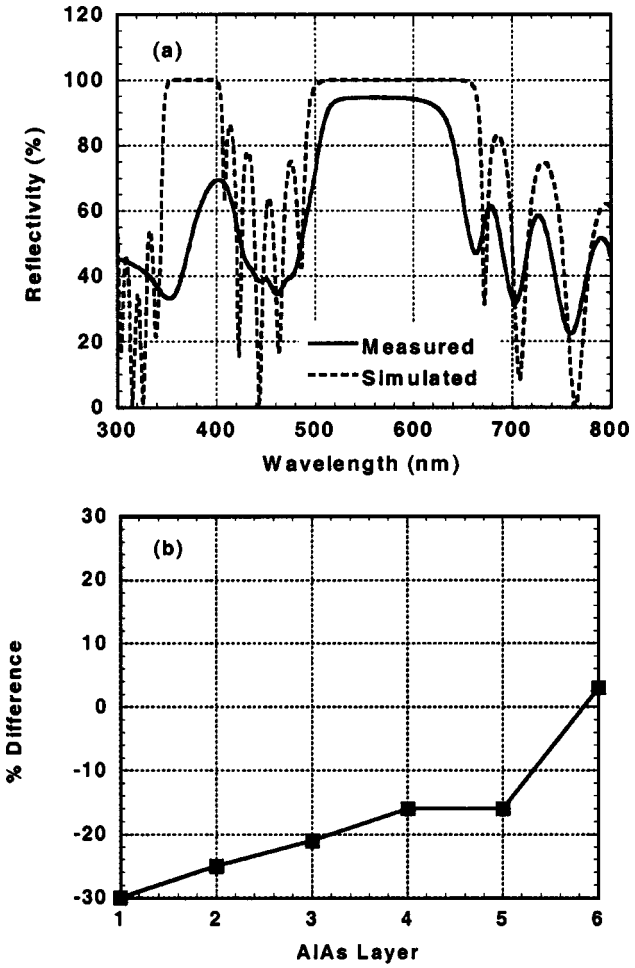

FIG. 2. Reflectivity spectra (a) for a 6 pair polycrystalline (Ga,P)/Al-oxide DBR using a $\lambda/4n$ oxide layer. Included is a spectra for the simulated DBR based on TEM thickness measurements. Note that the bandwidth of the curve closely matches the simulated case, but the maximum reflectivity is much lower due to thickness variations among the as-grown α-(Al,As) layers. (b) Thickness variation of the α-(Al,As) layers as a percent difference from the designed thickness. While the magnitude of the thickness variations are small, they represent a large percentage of the layer causing a reduction in the maximum reflectivity.

Possible causes of the thickness variations include temperature fluctuations in the substrate and an instability in the As-cracking cell at such low As overpressures. The substrate temperature variations would affect the sticking coefficients of the As at lower temperatures. Studies have shown that the sticking coefficient is nearly exponential with temperature at these low temperatures,[8] so a 10 °C variation in substrate temperature could affect the growth rates. Also, the As-cracking cell showed some instability in the As flux during growth. The valve position had to be constantly adjusted during growth of the AlAs layers to maintain a constant

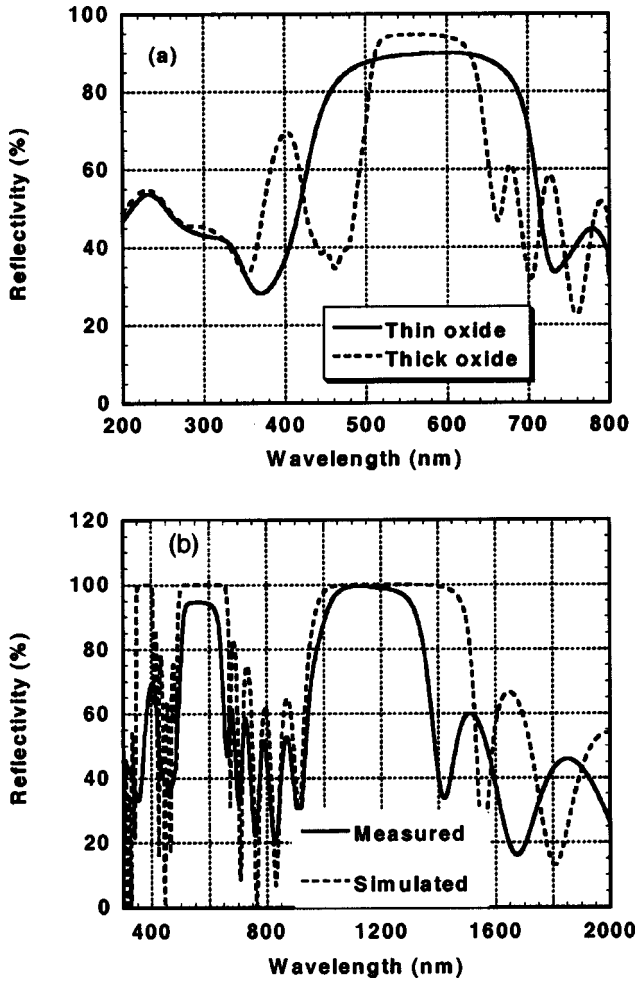

FIG. 3. Reflectivity spectra of (a) a 6 pair polycrystalline (Ga,P)/Al-oxide DBR using a $\lambda/4n$ and a $3\lambda/4n$ oxide layer. Note the improvement of the thicker DBR structure. This is due to the minimized effects of layer thickness variations. A wide range scan of the thicker DBR is shown in (b). The different design results in a spectrum that is highly reflective at two wavelengths, 550 and 1100 nm.

chamber pressure. In contrast, the flux of the P-cracking cell was very stable during the entire growth period. Because only the As-bearing layers show variability in thickness, it is likely that the cracker instability is the cause of the variations.

C. Effects of DBR design on reflectivity spectra

To minimize the effects of the AlAs thickness variations, a design using a $3\lambda/4n$ AlAs layer was used. It was thought that even with thickness variations, the percent variation between the designed and actual thickness in the AlAs layers would be minimized if the layers were three times thicker. The reflectivity and placement of the central wavelength should not be affected by the change in design. To test the improved design, a 6 pair 400 Å polycrystalline (Ga,P)/3396 Å α-(Al,As) DBR was grown and processed. Figure 3(a) shows the reflectivity spectrum of the new DBR as compared to the spectrum using the $\lambda/4n$ α-(Al,As) layer thickness. Note that the maximum reflectivity has increased to ~95%, a noticeable improvement over the previous design. The maximum reflectivity shown here is corrected to account for the losses in the trenches which were used to laterally oxidize the α-(Al,As). While an improvement was seen in maximum reflectivity, the bandwidth noticeably decreased due to the thicker (Al,As) layers.

In addition to the increased reflectivity of the DBR, a spectral measurement over a larger wavelength range indicated the presence of an additional highly reflective (>99.5%) band near 1100 nm as shown in Fig. 3(b). This additional highly reflective portion of the spectra is a result of the thickness designs of the DBR. By manipulating the design of the DBR, multiple passbands with great reflective efficiency can be achieved. While these two wavelengths cannot be reached using material systems lattice matched to GaAs, the possibility of III-nitride based material systems utilizing this multiband reflectivity is apparent. Through the use of band-to-band recombination as well as intersubband recombination,[9] the III-nitride material system could reach the two wavelengths proposed here while grown on the same host substrate.

Also shown in Fig. 3(b) is a difference in maximum reflectivity of the two highly reflective lobes. The decrease in reflectivity at the shorter wavelengths (95% versus 99.5%) is possibly caused by absorption of high-energy photons in the polycrystalline (Ga,P) or Al-oxide materials. The absorption in the (Ga,P) material is unlikely due to the indirect nature of the material, but these photon energies are near the Γ valley of the conduction band. The possibility of absorption in the oxide is present also due to the large amount of excess As in the oxide from the as-grown α-(Al,As). This phenomenon warrants further study.

IV. CONCLUSIONS

Using VLT-MBE growth techniques, the microstructure of the III–V compounds can be controlled between amorphous and polycrystalline material by manipulating the group-V overpressure. In addition the growth rate of the material is highly dependent on the group-V overpressure due to the high sticking coefficients of As and P at these low growth temperatures. A 6 pair $\lambda/4n$ polycrystalline (Ga,P)/$\lambda/4n$ Al-oxide DBR was designed and fabricated to reflect at a central wavelength of 550 nm. Thickness variations in the AlAs layers caused a reduction in the maximum reflectivity of the DBR. To combat this problem, a $\lambda/4n$ polycrystalline (Ga,P)/$3\lambda/4n$ Al-oxide DBR was fabricated which noticeably improved the reflectivity. In addition, the improved design for the DBR generated another highly reflective (>99.5%) band in the reflectivity spectrum near 1100 nm. The high reflectivities in the visible spectrum combined with the compliant nature of the material makes this DBR suitable for applications involving nitride based materials.

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